CHAPTER 4

CHAPTER OUTLINE

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Global Warming and Climate Change

ALTHOUGH SCIENTISTS HAVE STUDIED THE EARTH'S ATMOSPHERE SINCE THE BEGINNING OF THE TWENTIETH CENTURY, DURING THE PAST 20 YEARS THEIR UNDERSTANDING OF THE PROCESSES THAT TAKE PLACE IN THE ATMOSPHERE HAS GROWN MORE SOLID AND THEIR CLIMATE MODELS MORE SOPHISTICATED. Evidence that human behavior is affecting the climate of the Earth has become more certain, and even greater global warming is now expected to occur in the future. The proof that global warming is a result of human activity and that even more human-induced climate change is in store is presented in the latest report of the Intergovernmental Panel on Climate Change (IPCC), which was released in February 2008 (see http://www.ipcc.ch).

In its "Summary of Policymakers," the IPCC bluntly stated that "scientists are more confident than ever that humans have interfered with the climate and that further human-induced climate change is on the way." Clearly, we have caused global warming—yet the report does offer a note of optimism. Although we have harmed the climate of the Earth with our activities, the magnitude of global warming in the future depends on how seriously we choose to limit greenhouse gas emissions.

Four questions are addressed in this chapter: Which changes have been observed in the Earth's climate? Which components of our atmosphere are considered to be greenhouse gases? How do they cause climate change? What does the future hold?

Global Temperature from the Ice Ages to Present Time

Global climate is determined by energy. The amount of energy in the Earth's atmosphere can be changed in three different ways: (1) changes in the amount of solar radiation reaching the Earth (changes in the sun's output or the Earth's orbit), (2) changes in the fraction of solar radiation that is reflected (*albedo*), and (3) changes in the amount of infrared (IR) radiation that is radiated back into space.

Measurements of the output of the sun over recent decades show that solar output remains fairly constant, varying by only some 0.1%. Ice ages on Earth have occurred in regular cycles for the past 3 million years, and it appears as if they are linked to regular variations in the planet's orbit around the sun (known as *Milankovitch cycles*), rather than any variation in solar output. The Earth has gone through four glacial periods during the past 450,000 years, all of which were caused by gravitational attraction between the Earth and other planets in the solar system. It appears that if the inclination of the sun is not optimal, the amount of sunlight striking the northern continents in the summer is not sufficient to melt the snow that fell that year. If the snow from the past winter does not melt, an ice sheet starts to grow and glaciation begins. Computer climate models confirm that ice ages can be started this way; they also predict that the next such ice age will begin in approximately 30,000 years.

Once the Earth has absorbed solar radiation, to maintain an energy balance it must radiate, on average, the same of amount of energy back into space. The Earth does so by emitting IR radiation. A considerable amount of the outgoing IR radiation does not escape into space, however, but is reabsorbed by **greenhouse gases** in the atmosphere and then reradiated back to Earth. As a result of this absorption and reradiation, the atmosphere is warmed. The warming effect caused by the absorption and reradiating of IR radiation by the greenhouse gases is commonly called the **greenhouse effect**—a name that arose because the gases act somewhat like a pane of glass in a greenhouse. Visible light passes through the glass of a greenhouse and is absorbed by the objects inside. These objects are warmed and emit heat energy in the form of IR radiation, which cannot pass through glass. Thus this radiation is trapped and the temperature rises inside the greenhouse.

Atmospheric carbon dioxide concentration also plays an important role in the development of ice ages. Ice from polar regions can provide a history of atmospheric temperature and atmospheric CO_2 concentration at the time each ice layer was deposited. Antarctic ice core data, which can be seen in **Figure 4.1**, indicate that atmospheric CO_2 concentration is low (approximately 190 ppm) in the cold glacial times and high (approximately 280 ppm) in the warm interglacial times. It appears that small increases in surface temperature cause dissolved CO_2 to move from the ocean water into the atmosphere. In turn, the increased level of CO_2 in the atmosphere further increases warming by the greenhouse effect. When the surface cools, the atmospheric CO_2 redissolves in ocean water, which causes further cooling as the greenhouse effect is reduced. In this way, surface temperature and atmospheric CO_2 concentration have tracked each other for almost a half a million years.

Instrumental observations from 1850 to the present show that the global mean temperature of the Earth has risen during this period. As can be seen in **Figure 4.2**, this temperature changed very little from 1850 to 1915, but since then global warming has occurred in two phases. During the first phase (1910 to 1940), the global mean temperature rose 0.35°C; during the second phase (1970 to present), the global mean temperature rose 0.55°C. Eleven of the 12 warmest years on record occurred during the second phase, with 1998 and 2005 being the two hottest years on record. Measurements above the surface have shown that the troposphere has warmed at a slightly faster rate than the surface, while the stratosphere has cooled. Global warming has been confirmed by measurements that show the ocean temperature and sea level to be rising, and diminished snow cover in the northern hemisphere.

The Increase in Atmospheric Carbon Dioxide

Analysis of air trapped in samples of ancient ice shows that the average concentration of carbon dioxide in the atmosphere has been increasing for thousands of years. Twenty thousand years ago, the concentration of this gas in the atmosphere was approximately 200 ppm; before the beginning of the Industrial Revolution at the end of the nineteenth century, it had risen to about 280 ppm. In 1958, when measurements were first made at Mauna Loa in Hawaii, the atmospheric carbon dioxide concentration was 315 ppm; by 2000, it had reached 370 ppm **(Figure 4.3)** and in 2008, it reached 380 ppm. Thus there has been a 30% increase in atmospheric carbon dioxide in just 100 years. The major cause of this increase is the burning of fossil fuels by electric utilities, automobiles, and industry.

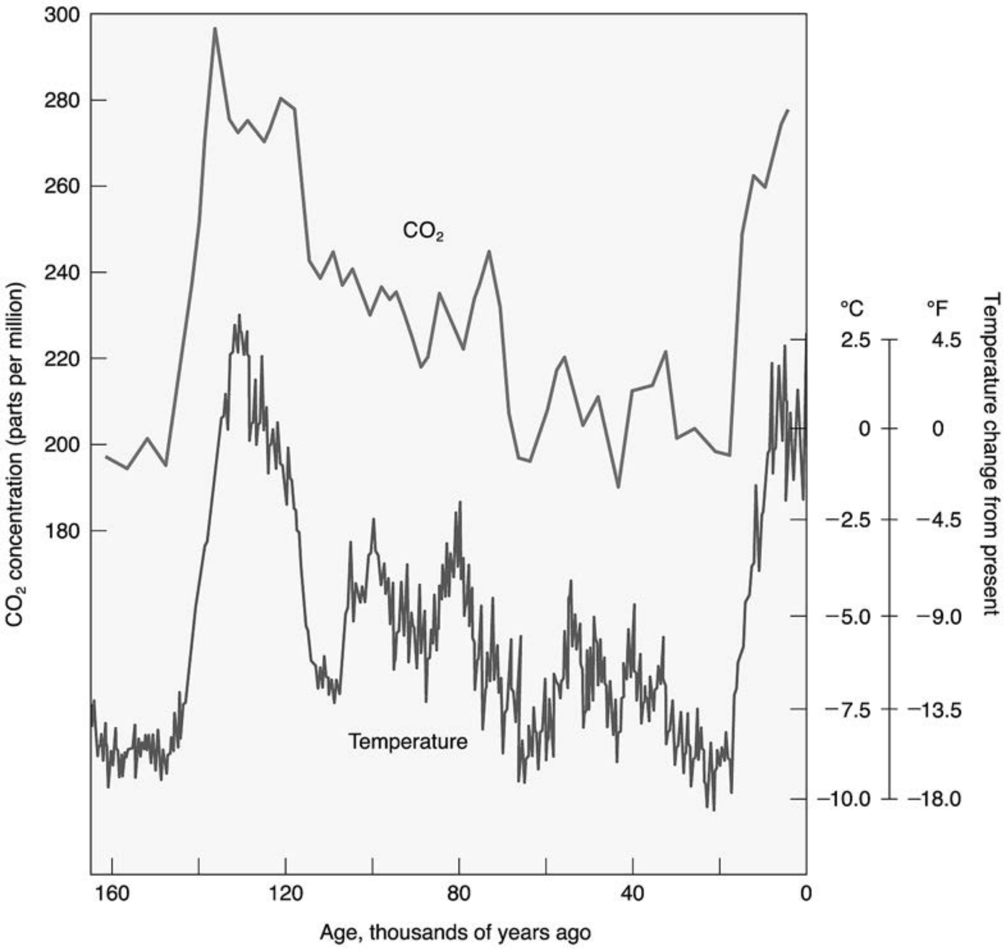

Figure 4.1 Variations in atmospheric carbon dioxide concentration and air temperature over the last 160,000 years were revealed by analysis of Antarctic ice cores. Air temperature has risen and fallen in step with increases and decreases in the carbon dioxide concentration.

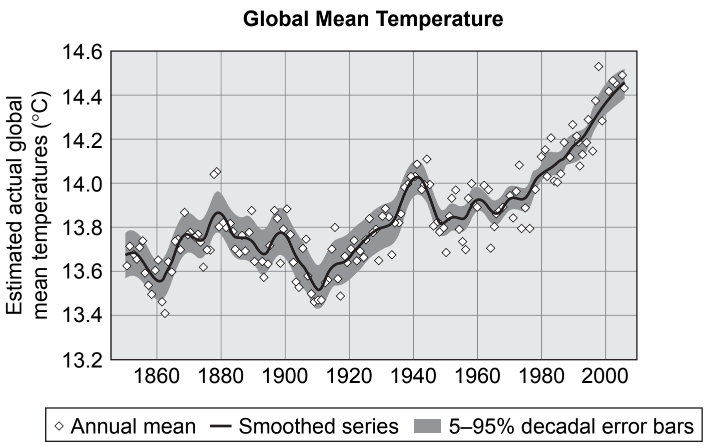

Figure 4.2 Annual global mean temperatures from 1850 to present.

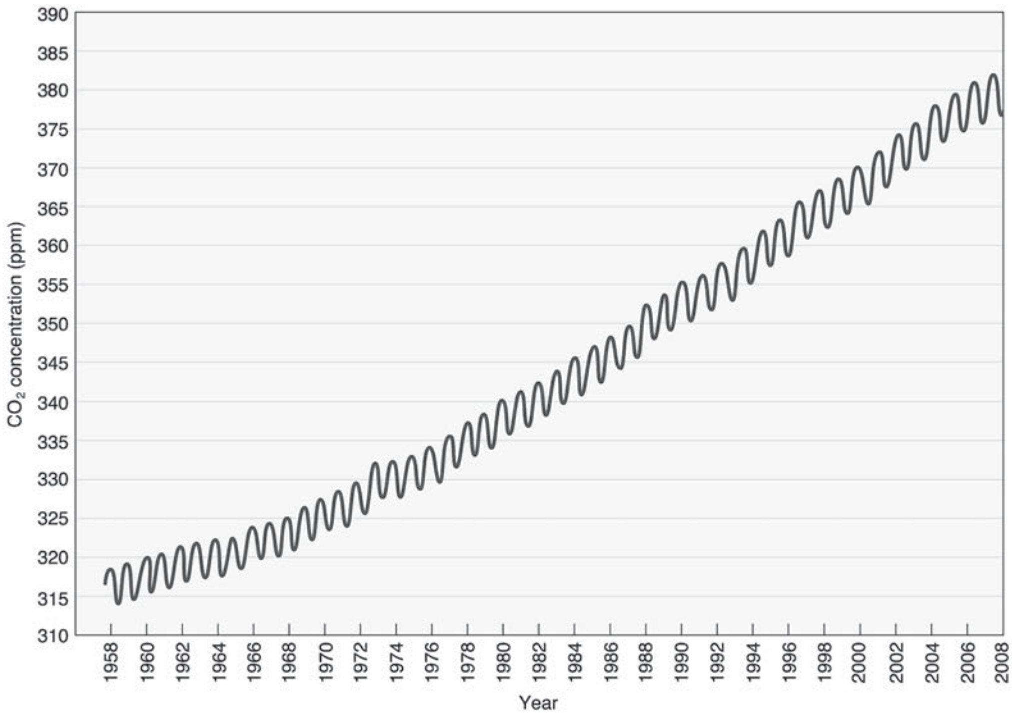

Figure 4.3 Since the first measurements were made at Mauna Loa, Hawaii, in 1958, the carbon dioxide concentration in the atmosphere has increased dramatically. The yearly seasonal variations are caused by the removal of carbon dioxide from the atmosphere by growing plants in the summer and the return of carbon dioxide to the atmosphere in the winter when plants decay.

A secondary cause of the increase is deforestation. As trees grow, they take carbon dioxide from the atmosphere during the process of photosynthesis; when they decay or are burned in forest fires, carbon dioxide is released back into the atmosphere. Any new growth in a cleared area, whether crops or grasses, takes much less carbon dioxide from the atmosphere than does a mature forest. By 2000, 2% of all rain forests were being cut and burned each year. Destruction is particularly severe in tropical rain forests, especially in Brazil.

Human activities produce four principal greenhouse gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and halocarbons. As can be seen in **Table 4.1**, these gases

Table 4.1

Properties of Anthropologic Greenhouse Gases

	CO_2	CH_4	N_2O	Freon-11	Freon-23
Atmospheric concentration	ppmv	ppbv	ppbv	pptv	pptv
Preindustrial (1750–1800)	~280	~700	~270	0	0
Current	370	1,745	314	268	14
Current rate of change/year*	1.5	7.0	0.8	−1.4	0.55
(% increase/year)	0.41	0.40	0.25	−0.52	3.92
Atmospheric lifetime (years)	5 to 200†	12	114	45	260

* Rate is calculated over the period 1990–1999.
† No single lifetime can be defined for CO_2 because of the different rates of uptake by different removal processes.

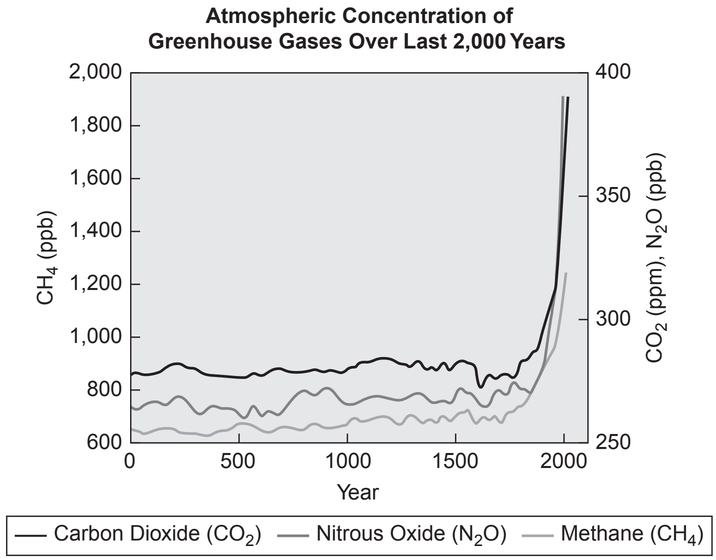

Figure 4.4 Atmospheric concentrations of long-lived greenhouse gases over the last 2,000 years.

accumulate in the atmosphere and their concentrations increase over time. The concentration of these gases in the atmosphere has increased especially significantly during the industrial era **(Figure 4.4)**, and their releases are directly related to human activities. Although their combined total concentration is considerably less than that of carbon dioxide, the other greenhouse gases absorb and re-emit more IR radiation, molecule for molecule, than does carbon dioxide. Methane, for example, is approximately 25 times more effective than carbon dioxide at trapping heat. If the levels of the other greenhouse gases continue to increase at the present rate, it is estimated that their warming effect will soon equal that of carbon dioxide.

The steady rise in methane's atmospheric concentration during the latter part of the twentieth century is attributed primarily to a worldwide increase in the number of cattle and the number of rice paddies, both of which are **sources** of methane. Other anthropogenic sources of methane include landfills and coal mines.

Nitrous oxide is formed naturally in the soil during microbiological processes associated with nitrogen fixation. Its increased concentration in the atmosphere is believed to be caused primarily by more widespread use of nitrogen-containing fertilizers.

Infrared Absorption and Molecular Vibrations

Infrared radiation is not energetic enough to break covalent bonds or to cause electronic transitions, but it can change the vibrational or rotational motion of a molecule. To absorb IR radiation, a molecule must undergo a net change in **dipole moment** as a result of its vibrational or rotational motion.

Monatomic inert gases, such as argon, which is the third most abundant atmospheric gas (with a concentration of 0.9%), do not have covalent bonds and, therefore, cannot absorb IR radiation. No net change in dipole moment occurs during the vibration or rotation of homonuclear species, such as N_2 and O_2. Because these molecules are symmetrical, no matter how much the covalent bonds are stretched, the dipole moment remains constant. As a consequence, these molecules, which are the principal constituents of the atmosphere, also cannot absorb IR radiation.

Other diatomic molecules, which contain two different atoms (such as CO), do absorb IR radiation. The frequency at which they do so can be estimated by assuming that the

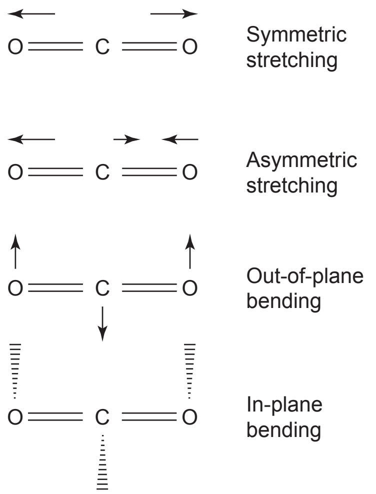

Figure 4.5 Vibrations of a CO_2 molecule: symmetric and asymmetric stretching and in-plane and out-of-plane bending.

atoms in the molecule are balls and the bond that connects them is a spring. The frequency of oscillation depends on the weight of the two atoms and the strength of the bond connecting them. This calculation assumes the molecule is a harmonic oscillator.

All of the gases that contribute to the greenhouse effect have three or more atoms (polyatomic molecules). Although it is possible to extend the harmonic oscillator equation to estimate the wavelength of absorption for polyatomic molecules, a different type of analysis will be used here to determine the absorption of atmospheric polyatomic molecules.

Carbon dioxide (CO_2), for example, is a linear triatomic molecule with a carbon atom in the middle and two oxygen atoms on its left and right, with each bonded by a double bond (O=C=O). Upon first examination, you might think there would be only one vibrational mode for CO_2, a stretching (and compressing) of the carbon oxygen double bond. In reality, because each double bond stretches independently, CO_2 has more than one IR absorption. As can be seen in **Figure 4.5,** CO_2 has two stretching vibrations and two bending vibrations. The arrows show the direction of motion of each atom. A **symmetric stretch** occurs when the two oxygen atoms both move outward and inward together while the carbon remains fixed. An **asymmetric stretch** occurs when one double bond is compressed while the other is stretched. Besides stretching vibrations, CO_2 can vibrate by bending. One bending vibration, which can be seen in Figure 4.5, occurs when bending occurs in the plane of the linear molecule; the other occurs when the atoms bend out of plane. IR radiation causes most polyatomic molecules, including the greenhouse gases H_2O, CH_4, and N_2O, to vibrate and absorb IR radiation.

The two most important greenhouse gases are the polyatomic molecules CO_2 and H_2O. Approximately 89% of the 34°K temperature increase resulting from natural greenhouse warming can be attributed to water, while carbon dioxide accounts for approximately 7.5% of the greenhouse effect. As can be seen in **Figure 4.6,** carbon dioxide represents the largest fraction of all greenhouse gas emissions in the United States and the world, with fossil fuel emissions representing the vast majority of CO_2.

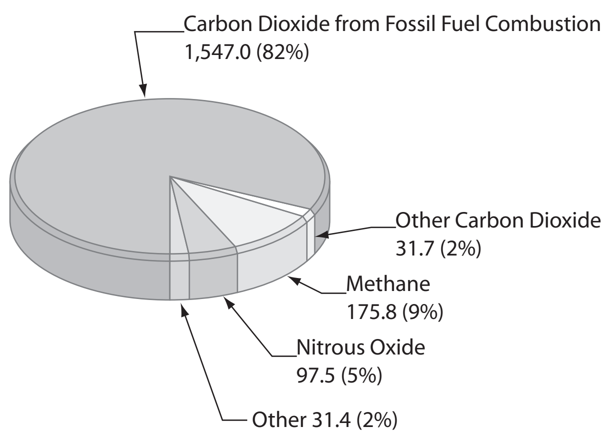

Figure 4.6 U.S. anthropogenic greenhouse gas emissions by gas in 2001 (million metric tons of carbon equivalent).

Residence Time of Atmospheric Gases

To assess the effect of any atmospheric gas on global warming, it is important to know how long the gas will remain in the atmosphere before it decomposes by one pathway or another. Each atmospheric gas has a **residence time (T_{res}),** which describes the average amount of time one of its molecules spends in the atmosphere. If the steady-state atmospheric concentration (*C*) is known and the rate of input (flux, *F*) of that gas is known, the residence time can be calculated as follows:

$$T_{res} = C/F$$

The average residence time of the CO_2, N_2O, and chlorofluorocarbons (CFCs) in the atmosphere is more than a century. Thus these gases, when emitted, will have an effect for a long, long time. Methane, by comparison, has a residence time of only approximately a decade.

EXAMPLE 4.1

What is the residence time of CH_4 if the current atmospheric concentration is 1.7 ppmv and the total release of methane from all sources is 550 million tons per year?

Solution

Either mass or concentrations of the gas can be used to solve this problem. Because we know the atmospheric concentration in ppm, we can express the rate in ppm by dividing the yearly input amount by the total mass of the atmosphere (5.27×10^{18} kg). The average mass of atmospheric gases is estimated to be 29 g/mol (an average of N_2 and O_2 molecular weights).

Step 1: Convert 550 million tons of methane released per year to kilograms (flux):

$$\frac{550{,}000{,}000 \text{ tons/year}\left(2{,}000 \text{ pounds/ton}\right)}{2.2 \text{ pounds/kg}} = 5.0 \times 10^{11} \text{ kg/year}$$

Step 2: Compute the number of moles of gas in the atmosphere:

$$5.27 \times 10^{18} \text{ kg} = 5.27 \times 10^{21} \text{ g}$$

$$\frac{5.27 \times 10^{21} \text{ g}}{29 \text{ g/mol}} = 1.82 \times 10^{20} \text{ mol}$$

Step 3: Compute the mass of methane in the atmosphere:

$$\left(1.82 \times 10^{20} \text{ mol}\right)\left(1.75 \times 10^{-6}\right) = 3.19 \times 10^{14} \text{ mol methane}$$

$$\left(3.19 \times 10^{14} \text{ mol}\right)\left(16 \text{ g/mol}\right) = 5.1 \times 10^{15} \text{ g} = 5.1 \times 10^{12} \text{ kg}$$

Step 4: Plug the values into the equation:

$$T_{res} = C/F = \frac{5.1 \times 10^{12} \text{ kg}}{5.0 \times 10^{11} \text{ kg/year}} = 10 \text{ years}$$

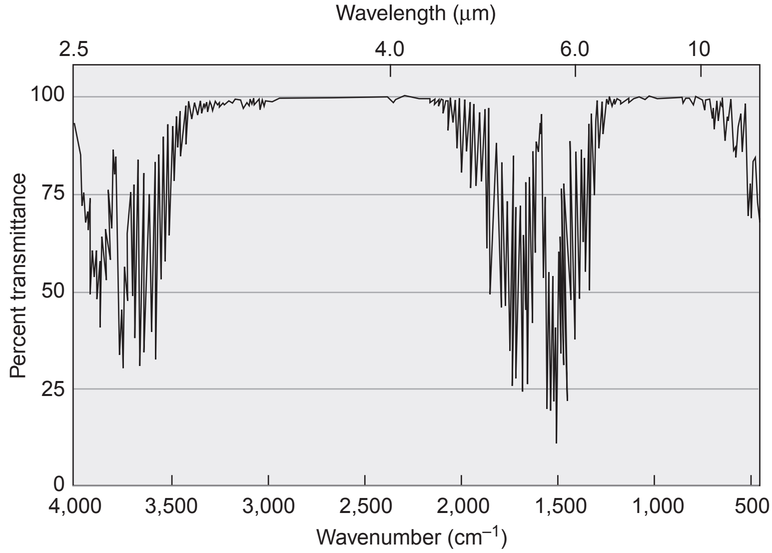

Figure 4.7 Infrared absorption spectrum of water [$cm^{-1} = 10{,}000/\lambda(cm)$].

Atmospheric Water Vapor

For Earth, water vapor is actually the most important greenhouse gas because it strongly absorbs radiation in the IR region. As can be seen in **Figure 4.7,** gaseous water strongly absorbs in two distinct IR regions: 2.5 to 3.4 μm and 10 to 13 μm. Water vapor is not listed as a constituent of air because its concentration in the atmosphere varies greatly depending on location and temperature. Water vapor, on average, has approximately a 0.4% concentration in the Earth's atmosphere. It is involved in two important feedback processes that oppose each other. A **positive feedback** cycle occurs when global warming increases evaporation from oceans, which in turn leads to higher concentrations of water vapor in the air. The increased amount of water vapor causes more infrared to be absorbed, which then increases warming of the Earth's surface. A **negative feedback** cycle occurs when the troposphere becomes cloudier, which causes more reflection of incident solar flux and, in turn, cooling of the Earth's surface. Because there are no **anthropogenic** (made by humans) activities that directly cause any increase in the concentration of water vapor in Earth's atmosphere, it is not usually listed among the greenhouse gases. Other greenhouse gases have their own feedback loops.

Atmospheric Carbon Dioxide

There is no doubt that carbon dioxide contributes to greenhouse warming. As can be seen in **Figure 4.8**, carbon dioxide absorbs radiation in three IR regions; that is, it has a very strong absorbance in the 14- to 19-μm range, a strong absorbance in the 4- to 4.5-μm range, and a weak absorbance in the 3-μm range. If the Earth's IR emission spectrum is superimposed on the IR absorption spectra of carbon dioxide and water vapor, the result (shown in **Figure 4.9**) indicates that the combined IR absorption of carbon dioxide and water coincide with most of the IR emission from the Earth. A unobstructed region of the spectrum occurs between 7.5 and 13 μm, through which IR radiation from the Earth's surface can still escape. This section of the IR is called the **atmospheric window.**

Emissions from the burning of fossil fuels are the primary anthropogenic source of CO_2. The carbon stored in fossil fuels had been sequestered for millions of years beneath the surface of the Earth before the CO_2 was released through the combustion process. Natural sources of

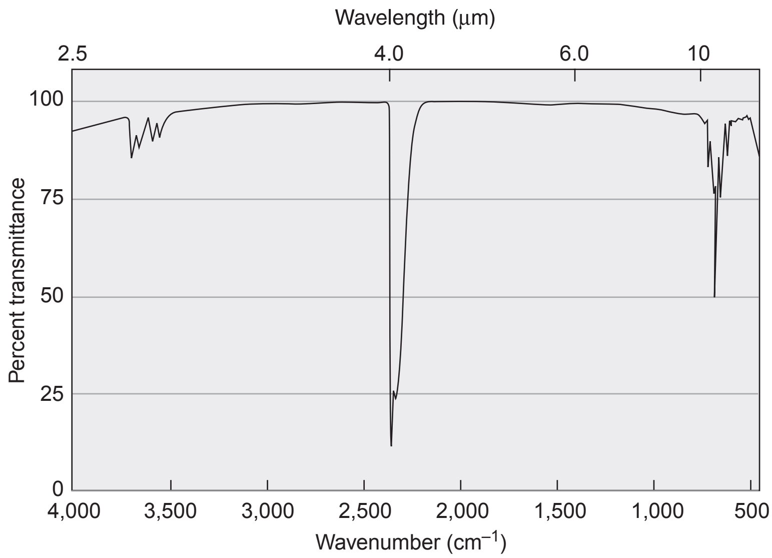

Figure 4.8 Infrared absorption spectra of carbon dioxide [cm^{-1} = 10,000/λ(cm)].

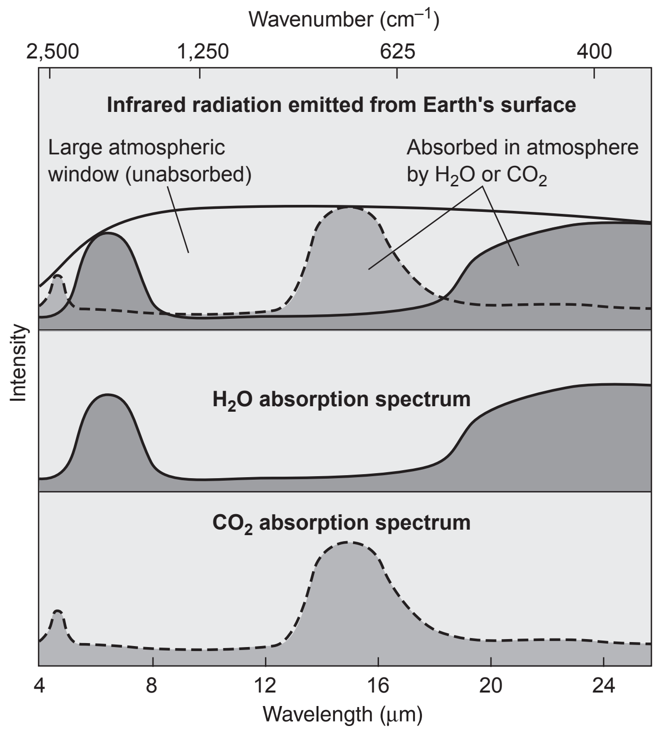

Figure 4.9 Absorption of radiation emitted from the Earth's surface by carbon dioxide and water vapor.

atmospheric CO_2 include the decomposition of organisms, plant and animal respiration, and some oceanic processes.

Light-duty vehicles (automobiles and pickup trucks) emitted 31% of all U.S. greenhouse gas emissions in 2001 and have been the fastest-growing source of CO_2 emissions in the United States since 1990. In 2011, the Environmental Protection Agency and the Department of Transportation's National Highway Traffic Safety Administration announced a national program to reduce greenhouse gas emissions from light-duty vehicles under the provisions of the Clean Air Act. Light-duty vehicles for model years 2012–2016 will have new Corporate Average Fuel Economy standards. By 2016, an automobile manufacturer's fleet must attain a fuel economy of 33.5 mi/gal, which will limit the average emission of CO_2 from the 2016 vehicles to 250 g per mile.

Several important CO_2 **sinks,** which are mechanisms that remove CO_2 from the atmosphere, operate on planet Earth. The sedimentary rock formation (*lithification*) that creates limestone ($CaCO_3$) represents by far the largest sink, but because the process of lithification requires an enormously long time to remove the CO_2 from the atmosphere, we will not consider it to be important in mitigating the anthropological greenhouse effect.

On a human time scale, the oceans represent the largest CO_2 sink. The oceans are a tremendous reservoir in the global carbon cycle. The first way oceans remove CO_2 from the atmosphere is by dissolving the gas (solubility pump). The cold polar ocean water at the surface dissolves atmospheric CO_2; the CO_2-rich surface water then sinks into the deep ocean, where it sequesters the CO_2 for several hundred years. This sink is expected to become less important as polar regions become warmer. The second way the oceans remove atmospheric CO_2 is biologically (*biological pump*). Marine phytoplankton take in atmospheric CO_2 and subsequently release carbon in a form that sinks to the ocean floor, where it is sequestered indefinitely through the lithification of sedimentary rocks. This process is estimated to reduce the atmospheric CO_2 concentration by one third of what it would be otherwise. Some scientists have suggested that fertilizing the ocean surface with iron sulfate might allow marine phytoplankton to reproduce more rapidly and remove even more CO_2. Although laboratory-scale iron fertilization experiments have verified that Fe is a limiting nutrient, its effect is short-lived, and the amount of new production exported from the surface layer is small. In addition, this approach would require continuous seeding of vast areas with outrageous amounts of Fe, which may cause unknown harm to existing marine ecosystems.

Other atmospheric sinks play minor roles compared to the oceans. For example, soils sequester atmospheric CO_2 by containment of partially decomposed organic matter known as humus. While the total amount of CO_2 sequestered in soil is unknown, improved soil conservation practices are anticipated to help mitigate the buildup of atmospheric CO_2 at least slightly. Another sink is the nonsoil component of the biosphere, vegetation, which absorbs CO_2 during photosynthesis and stores carbon in its biomass as it continues to grow. Only 30% of the Earth's surface is land, and only 30% of that land is covered by forests; thus the uptake by vegetation is a far smaller sink than the ocean and slightly smaller than the soils. Within the biosphere, the most critical region for sequestration is the tropical rain forest, which is rapidly disappearing.

Atmospheric Methane

The IR radiation in the atmospheric window can be absorbed by other polyatomic molecules. Because these molecules are composed of different atoms, they vibrate at different frequencies and as a result will absorb IR in different regions of the spectrum.

Methane (CH_4) is a polyatomic molecule with a tropospheric concentration of 1.75 ppmv (1,745 ppbv). Before 1750, the atmospheric methane concentration was 0.75 ppmv (750 ppbv), but during the industrial era, its concentration in the atmosphere increased steadily. In the mid-twentieth century, its concentration increased at a rate of approximately 0.5% per year. In the early 1990s, the rate of increase declined; since then, the rate of increase in the atmospheric methane concentration has been zero. The rise in atmospheric CH_4 has been associated with human activity and fossil fuel use, but the reason why the rate of increase of atmospheric CH_4 today has fallen to zero is not well understood. Because this gas's concentration is affected by both the rate of CH_4 release (sources) and the rate of CH_4 removal (sinks), a change in either factor will affect atmospheric CH_4 concentration.

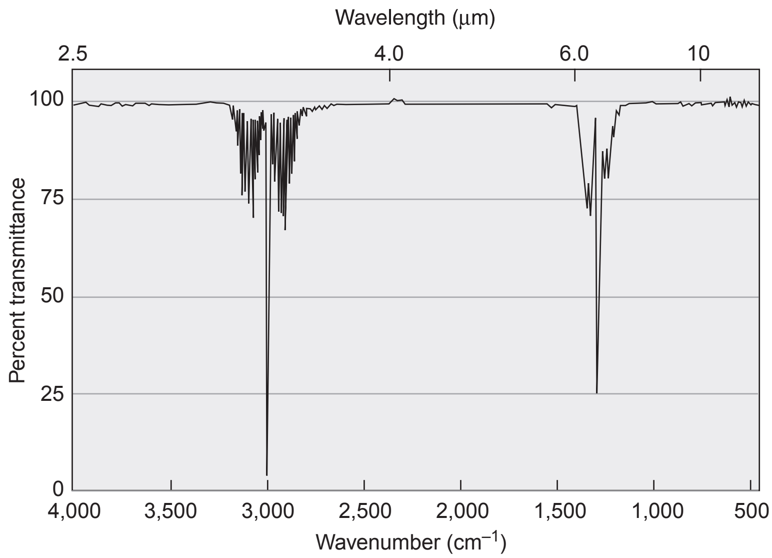

Figure 4.10 Infrared absorption spectrum of methane [$cm^{-1} = 10{,}000/\lambda(cm)$].

Neither the rate of release nor the rate of removal can be measured easily, which illustrates the overall difficulty facing atmospheric scientists trying to understand the complicated processes acting in our atmosphere.

As can be seen in **Figure 4.10,** methane absorbs IR in the 3 to 4 μm and 7 to 8.5 μm regions. Methane's absorption in the 3 to 4 μm range is not as important because the radiation from the Earth (black body radiation) hardly has any emission in this region. The absorption between 7 and 8.5 μm is within the atmospheric window, however, and through this absorption, methane can contribute to the greenhouse effect.

The sources of atmospheric methane have been understood only for the last three decades **(Figure 4.11).** Methane is released to the atmosphere through anaerobic decomposition, which is the decomposition of organic material in the absence of oxygen.

During the process of anaerobic decomposition, cellulose is converted into CH_4 and CO_2. Such anaerobic decomposition occurs readily in a waterlogged environment. On a global basis, approximately 23% of the atmospheric CH_4 is released naturally from wetlands, including bogs, tundra, and swamps, where methane-producing bacteria thrive in the rich organic matter (with a low oxygen content). The next leading source, accounting for approximately 20% of CH_4 releases, is from the flooding of rice fields, where certain types of bacteria also thrive. A

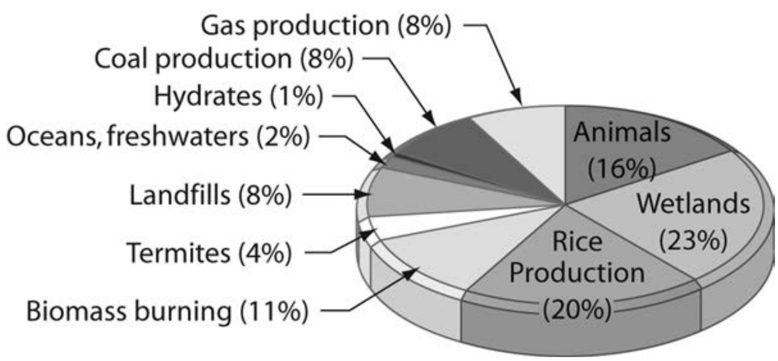

Figure 4.11 Sources of net global emission of atmospheric methane. Data from W.S. Reeburg, *Global methane budget studies*. 1996. IGACtivities Newsletter No. 6, September 1996. The International Global Atmospheric Chemistry (IGAC) Project. NOAA/OAR/PMEL.

third major source of CH_4 is from the bacteria present in the anaerobic digestive process of animals, particularly ruminants (cattle, camels, sheep) and certain species of termites. The inefficient digestion of ruminants releases 16% of the atmospheric CH_4, whereas termite mounds release another 4%. Methane emission from ruminants and rice fields is considered to be anthropogenic because ruminants are raised and rice is cultivated for human needs.

Several anthropogenic sources of methane are also found in the troposphere. CH_4 is released when natural gas pipelines rupture or leak. It is estimated that 1.5% of all methane carried in pipelines today is lost to the atmosphere. Although this may seem like a very high leakage rate, it is lower than in earlier times. Twenty years ago, natural gas pipelines in the former Soviet Union leaked methane at a much higher rate than today. At oil refineries, methane that has been dissolved in crude oil for thousands of years is released during the refining process; it may then be released into the atmosphere. Also, during the mining of coal, CH_4 that was trapped for centuries in the solid coal is released into the air. Another major anthropogenic source (16%) of atmospheric CH_4 is anaerobic decomposition of garbage in landfills.

The most important sink for CH_4 is its oxidation by hydroxyl radicals in the troposphere:

$$CH_4 + {}^{\cdot}OH \rightarrow {}^{\cdot}CH_3 + H_2O$$

Secondary sinks include soils that take up CH_4 and the transfer of CH_4 from the troposphere to the stratosphere.

There is great concern that the rate of methane release could increase in the future as a result of a temperature increase from the greenhouse effect. As the greenhouse effect raises the temperature of the Earth, the rate of anaerobic decay in swamps would increase and, therefore, more methane would be released. In turn, the additional methane in the atmosphere would absorb IR radiation and itself cause a further rise in temperature. This is an example of positive feedback, in which a series of events accelerates the rate of change.

A large quantity of methane also remains frozen in the permafrost of the subarctic regions. It was produced by the decay of plant material during warmer periods, when they became trapped during the last ice age. Western North America and eastern Siberia were not covered in glaciers during the last ice age. Nevertheless, the climate was very cold with powerful winds that caused rivers to move huge quantities of silt that settled in the lowlands of Alaska and Siberia. The top layer of this soil thawed during the summer and grass grew on it, capturing CO_2. When the bitter winter came, it froze the grass before it could decompose. Over the years, layer after layer of permafrost built up. In 2009, Canadian scientists estimated that approximately 1.7 trillion tons of carbon is held in soils, with approximately 88% of it being locked in permafrost. This amount is about 2½ times the amount of carbon in the atmosphere today. An increase in global temperature seems to be starting the melting of some permafrost, which will release the trapped methane. Measurements made in southern Alaskan lakes in 2011 reveal the formation of methane bubbles beneath the iced-over surface. Scientists estimate that if global warming continues, we can expect the permafrost in Alaska to begin thawing during the 2020s. The release of methane from permafrost would, in turn, further accelerate the rate of global warming as the released methane absorbs IR radiation.

Even larger quantities of methane are trapped at the bottom of the oceans in the form of methane hydrate, which has the formula $CH_4 \cdot 6\ H_2O$. Under high pressure and low temperature, this CH_4 is surrounded by a cage of water molecules. $CH_4 \cdot 6\ H_2O$ is an example of a **clathrate**, in which a small molecule occupies a vacant space in the center of a three-dimensional cage of water (ice) molecules. Greenhouse warming of the oceans, if it extends to their bottoms, could cause the release of methane from methane hydrate. It is possible that these positive feedback mechanisms could combine to release large amounts of methane that would begin a runaway greenhouse effect that would threaten all life on Earth.

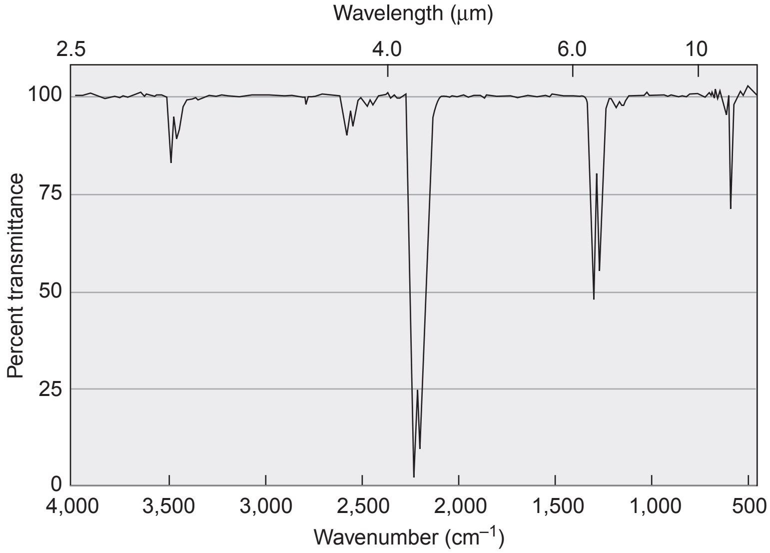

Figure 4.12 Infrared adsorption spectrum of nitrous oxide [$cm^{-1} = 10{,}000/\lambda(cm)$]. © Bio-Rad Laboratories, Inc., Informatics Division, Sadtler Software & Databases, 1980–2008. All rights reserved.

Atmospheric Nitrous Oxide

Figure 4.12 shows that nitrous oxide absorbs IR radiation in the 3 to 5 μm and 7.5 to 9 μm regions. The 7.5 to 9 μm absorption falls in the atmospheric window. This concentration of nitrous oxide in the atmosphere is 314 ppbv and is increasing by approximately 0.3% per year.

The major source of nitrous oxide is release from soil, lakes, and oceans by microbial denitrification of nitrate. It is difficult to determine how much of this release is natural and how much is caused by anthropogenic events. The application of synthetic nitrogen fertilizers increases the concentration of nitrate in the soil, which facilitates the microbial decomposition reaction. There are no important troposphere sinks for N_2O; as a result, it has a long tropospheric residence time—an estimated 120 years.

Atmospheric Chlorofluorocarbons

Chlorofluorocarbons are also greenhouse gases. **Figure 4.13** shows that CFCs such as Freon 12 absorb strongly radiation in the atmospheric window between 9.5 and 11.5 μm. The concentration of Freon 12 in the atmosphere exceeds 1 ppbv, and until the signing of the 1987 **Montreal Protocol**, its concentration was increasing at a rate of 5% per year. Because of the Montreal Protocol, some of the more developed countries (including the United States) have banned the manufacture and use of Freon 12, and its rate of increase in the atmosphere has slowed. The Montreal Protocol allows less developed countries, such as Mexico, to continue the manufacture and use of CFCs. As a result, Freon 12 is now one of the most smuggled materials into the United States, lagging only behind illicit drugs. The Montreal Protocol has called for a phase-out of the manufacture of all CFCs by 2010.

Fully fluorinated CFCs do not readily decompose, having lifetimes of thousands of years in the atmosphere. Even if the rate of CFC release decreases, these molecules will remain in our atmosphere for generations. The recently developed hydrochlorofluorocarbons (HCFCs) also absorb radiation in the same IR window and are greenhouse gases. The C—H bond in the HCFC is easier to break because it has a lower enthalpy (413 kJ/mol) than does the C—F bond (485 kJ/mol), so the HCFC decomposes more quickly than the CFC. Fortunately, the HCFCs' resonance times in the troposphere are considerably shorter than those of the CFCs.

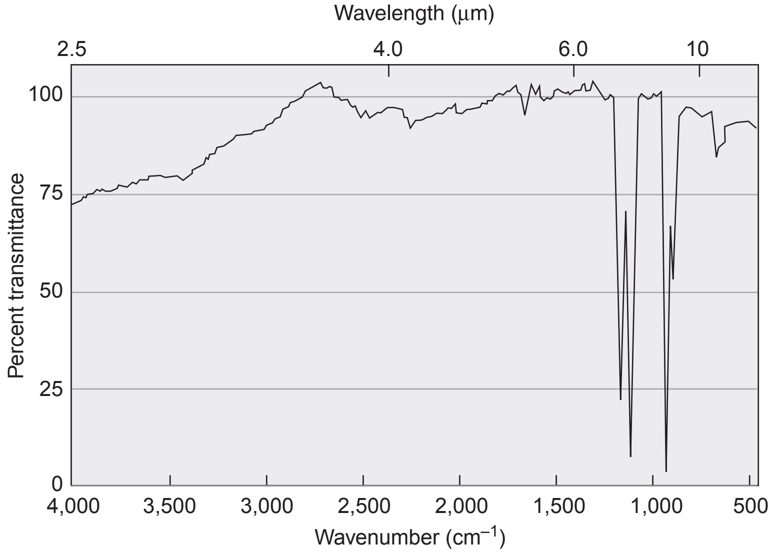

Figure 4.13 Infrared adsorption spectrum of CFC-12 [$cm^{-1} = 10{,}000/\lambda(cm)$].

Radioactive Forcing

All of the greenhouse gases discussed are present at some concentration in the Earth's atmosphere, and they all absorb IR radiation. Each absorbs IR radiation at different wavelengths and with different efficiencies, however. To assess the effect each greenhouse gas exerts on the atmosphere, the relative **radiative forcing** is a unit used to compare the relative contribution to the IR absorption per molecule added to the atmosphere. Three factors determine radiative forcing:

1. The concentration of the gas in the atmosphere today (and its residence lifetime in the atmosphere)
2. The wavelengths at which the gas molecules absorb radiation
3. The intensity of the absorption per molecule

The relative radiative value for carbon dioxide is arbitrarily set at 1, and the values for other gases are expressed relative to this value. Table 4.1 shows that the relative radiative forcing from CFCs is thousands of times greater than that of CO_2. This difference arises because the intensity of the CFCs' IR absorption is large and CFCs have a very long atmospheric lifetime. The contribution of N_2O is greater than CH_4 mainly because it has a longer lifetime. Moreover, methane is removed from the troposphere by a reaction with hydroxyl radicals, whereas N_2O is not removed in the troposphere; it drifts to the stratosphere, where it is decomposed when irradiated by intense ultraviolet rays at the upper altitudes.

Radiative Forcing Caused by Human Activity

The effect of human activities on radiative forcing since the beginning of the Industrial Revolution in 1750 can be seen in **Figure 4.14.** Because they all absorb IR radiation, the forcings for all greenhouse gases are positive. Decreases in stratospheric ozone concentration have caused cooling, while increases in troposphere ozone concentration have caused warming.

Aerosol particles affect radiative forcing in two ways: (1) Aerosols can reflect incoming solar radiation, which causes negative forcing; and (2) they can absorb IR radiation that would be lost from the surface of the Earth, which causes positive forcing. Some aerosols, such as soot (which is mostly carbon), strongly absorb radiation, whereas others such as sulfate aerosols are highly reflective. If radiative forcing for all aerosols is summed, the effect of aerosols is negative.

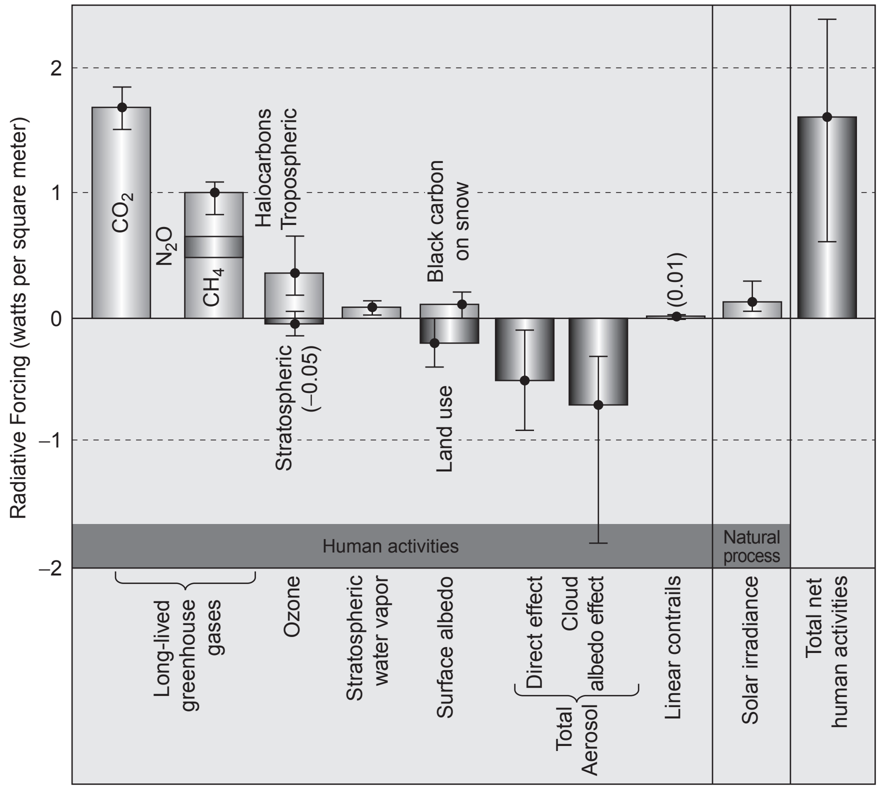

Figure 4.14 Radiative forcing of the climate between 1750 and 2005. Modifed from Solomon, S, et al. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, 2007, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Human activity, which has produced more soot, also has changed the albedo of the surface of the planet through changes in farming and forests. Human activity probably has changed the reflectivity of ice and snow as well. Experts suggest that more solar radiation is now being reflected from the surface of the Earth (negative forcing). Aircraft exhaust (**contrails**) can reflect incoming solar radiation while absorbing outgoing IR radiation. Aircraft contrails increase the Earth's clouds and have a small positive radiative forcing.

Radiative Forcing Caused by Nature

Changes in solar radiation and volcanic eruptions are the two major events that affect radiative forcing. Solar output has increased gradually during the industrial era, causing a small positive radiative forcing. Volcanic eruptions have historically caused a negative forcing for two to three years after an eruption. The last major volcanic eruption was Mount Pinatubo in 1991, and at the present time there is no volcanic aerosol causing radiative forcing.

The radiative forcing caused by nature today is about the same as it was in 1750, and this effect is very small compared to the differences in radiative forcing that have resulted from human activities. In our atmosphere, it is clear that the radiative forcing caused by human activities contributes much more to future climate change than does the radiative forcing caused by nature.

■■Evidence for Global Warming

Evidence for global warming is considerable. Glaciers all over the world have been retreating steadily for many years, and unusually large icebergs have been breaking off Antarctic ice shelves. The average temperature at the Earth's surface has increased by 0.3°C to 0.6°C (0.5°F to 1.1°F) since the last half of the nineteenth century. During the same period, sea levels around the world have risen 10 to 25 cm (4 to 10 inches), as water has expanded and ice has melted. The 14 warmest years since 1860 (when reliable recordkeeping began) have all occurred since 1980; 1998 and 2005 were the hottest years on record (Figure 4.2). The rate of temperature increase in the twentieth century was greater than at any time since 1200 A.D.

Recent studies of ancient ice have provided convincing evidence that the warming trend is likely to continue if carbon dioxide emissions continue to rise. Scientists took mile-long ice cores, dating back 160,000 years, from Antarctic glaciers and analyzed the air trapped in pockets in the ice for carbon dioxide. They also estimated the air temperature at the time the air became locked in the ice, using a technique based on measurements of the ratio of deuterium (^2_1H) to ordinary hydrogen (^1_1H) in the ice surrounding the air pockets. Lighter water molecules evaporate more readily than heavy water molecules. Therefore, the higher the $^2_1H/^1_1H$ ratio in the frozen water, the higher the temperature. From these data, the scientists were able to estimate temperatures at the time the different layers of ice were formed. As Figure 4.1 shows, a remarkable correlation exists between carbon dioxide concentration and air temperature. The air temperature rises and falls in step with the increases and decreases in the carbon dioxide concentration.

Computer-generated climate models also predict a warming trend. These models are based on numerous complex mathematic equations representing the many variables that affect climate. The information is fed into supercomputers, which then project temperature changes that are likely to occur if atmospheric carbon dioxide increases. Because many factors, such as the influence of clouds and the role of deep ocean currents, are not well understood and are not included in the computer models, some scientists have been skeptical about global warming. Nevertheless, in 2007, the IPCC—a group of 2,500 scientists from 100 countries—concluded that "the balance of evidence suggests that there is a discernible human influence on global climate."

Two recent advancements have improved our ability to predict global climate changes. The first is the coordination of 18 different groups of climate scientists from around the world, each of which has created its own computer model for the factors that control the Earth's climate. Some climatic processes, such as the flow of the ocean and the propagation of sunlight and heat, are well understood and well represented by traditional models. Others, such as the formation and movement of clouds and the flow of ocean eddies, are still being studied and their effects need to be estimated. Models approximate the effects of each of these factors using simplified equations called **parameterizations.** The use of so many different models by the IPCC is unprecedented in climate studies and has allowed the IPCC to quantify the effects of uncertainties in climate processes and use these data to improve its confidence in predicting global climate changes.

The second advance is the fact that climate scientists now better understand the complex processes that occur on Earth. The behavior of aerosols, the movement of sea ice, and the exchange of water and energy between land and atmosphere, for example, are now much better understood than they were 20 years ago.

The IPCC studies show two major patterns that attribute global warming to human activity. The first pattern of change is the observation that greater warming of the atmosphere is occurring over land than over the ocean and that the surface of the ocean is warmer than deeper ocean water. This pattern is consistent with warming caused by greenhouse gases in the atmosphere above both land and ocean. A second pattern of change is the observation that although the troposphere has warmed, the stratosphere just above it has cooled. If an increase in radiation from the sun was the cause of global warming, then the temperatures of both the stratosphere and the troposphere would be expected to increase. Instead, the observed warming of the troposphere is consistent with an increase of the concentration of greenhouse gases there, whereas the observed cooling of the stratosphere is consistent with the destruction of ozone there. The collected climatic data, when statistically analyzed, provide the base for the increased confidence that human activities are the cause of global warming.

Effects of Global Warming

The effects of global warming could be devastating. The IPCC predicts that if nothing is done to lower emissions of greenhouse gases, by 2100 the average global surface air temperature on the Earth will increase by as much as 1°C to 3.5°C (1.8°F to 6.3°F), and world sea levels will rise by 15 to 90 cm (6 to 36 inches). These may seem like small increases, but we should remember that at the time of the last ice age, the Earth's temperature was only 5°C lower than it is today. A sea level rise of only 15 cm (6 inches) would cause flooding in many coastal areas.

With rising temperatures, air circulation, ocean currents, and rainfall patterns would change, causing generally violent weather. As a result, some regions of the world, including much of the United States, would experience droughts, while other regions would become much wetter. Ecosystems all over the world would be disrupted, and some species might face extinction. Climate-related diseases such as malaria might attack areas where they are currently unknown.

The IPCC also points out that, in addition to global temperature increases, our ecosystem could experience a variety of effects:

1. Water
   a. Increasing water availability in moist tropics and high latitudes
   b. Decreasing water availability and increasing drought in mid-latitudes and semi-arid latitudes
   c. Melting of glaciers, polar icecaps, and polar sea ice
   d. Rising sea levels that threaten to flood Pacific Islands
2. Ecosystems
   a. As many as 30% of species at increasing risk of extinction
   b. Increased coral bleaching
   c. More species shifting their ranges to cooler locales
   d. Increased wildfire risk
3. Food
   a. Negative impact on subsistence farmers
   b. Decreased cereal productivity in low latitudes
   c. Negative impact on subsistence fishers
4. Coasts
   a. Increased damage from floods and storms
   b. Loss of approximately 30% of all coastal wetlands
   c. Increased risk of coastal flooding
5. Health
   a. Increasing burden from malnutrition, diarrhea, and infectious diseases
   b. Increased morbidity from heat waves, floods, and droughts
   c. Shift in location of disease vectors (mosquito-borne diseases)

Slowing Global Warming

Because of its potential to change world climate, global warming is viewed by scientists in many nations as the major environmental problem of the twenty-first century. The first treaty to address this problem was signed at the United Nations Conference on the Environment (the Earth Summit) in Rio de Janeiro, Brazil, in June 1992. The treaty set goals to reduce emissions of carbon dioxide and other greenhouse gases by industrialized nations to 1990 levels by 2000. However, because the proposed reductions were not binding, they were not met.

At a 1998 conference on climate change held in Buenos Aires, Argentina, 106 nations (including the United States) agreed to begin implementing the agreement reached the year before at Kyoto, Japan. The market-based Kyoto Protocol committed the 38 industrialized nations, including the republics of the former Soviet Union, to reducing global greenhouse gas emissions to at least 5% below 1990 levels by 2012. Different nations have different targets and timetables. The major flaw in the Kyoto Protocol is that it did not require cuts by the developing nations, most of which, including India and China, are opposed to making any reductions in the near future. An encouraging sign was Argentina's and Kazakhstan's voluntary agreement to reduce their greenhouse gas emissions. Although developing countries currently produce one tenth as much carbon dioxide per person as industrialized countries, in the last 10 years, as their economies have grown, their emissions have increased 75%. It is predicted that even if the industrialized nations reach their targets, the total concentration of greenhouse gases in the atmosphere will continue to rise.

Taking steps to reduce emissions will be both difficult and costly. In the United States, there is opposition from the oil and coal industries and their supporters in Congress, many of whom continue to deny the evidence for global warming. As a result, the Kyoto Protocol has not been ratified by the U.S. Senate. In the last decade, a group of major corporations launched the nation's first trading program for air pollution credits earned by firms that exceed emission-reduction goals. Launched in 2003, the Chicago Climate Exchange marks an expansion of the market-based steps to reduce greenhouse gas emissions. Under this system, which is patterned after commodity exchanges and similar in design to those implemented in Britain and Denmark, companies that exceed the reduction goals could sell their excess reductions to other companies that have not met average greenhouse gas emission standards. The Chicago Climate Exchange has proposed establishing ways of measuring greenhouse gas reductions. Some methods are direct, such as changes in the industrial process that reduce carbon dioxide emissions. Others are indirect and involve controversial "offsets," such as increased planting of forests or farms that absorb carbon dioxide. Critics of this approach say that by buying credits, big carbon dioxide emitters can avoid the reductions mandated by the Kyoto Protocol.

We can respond to climate change in one of two ways: We can adapt and learn how to live in a much warmer world, or we can act to mitigate the rise in temperature by reducing the release of greenhouse gases into the atmosphere. Because global temperatures are already on the rise, continued unabated release of greenhouse gases would cause catastrophic increases in global temperature. A combination of **adaptation** and **mitigation** will be necessary to control the rise in global temperature.

The IPCC considered six scenarios of economic expansion, population growth, and fossil fuel use in its 2007 report. These studies concluded that the concentration of greenhouse gases will rise from 445 ppm to 1,130 ppm, and that this higher level would cause a corresponding increase in temperature from 2.0°C to 6.1°C over preindustrial levels. To keep the temperature increase to a minimum, the IPCC recommends that the world stabilize atmospheric greenhouse gases at 445 ppm by 2015. If it does not, according to this expert panel, the world will face severe flooding in some local regions and severe drought in others, extinction of some species, and an overall economic disaster.

The IPCC report examined the most promising policies for holding the concentration of greenhouse gases at 445 ppm. The IPCC recommends the following:

1. Energy Supply
    a. Reductions in fossil fuel subsidies
    b. Taxes (carbon charges) on fossil fuels
    c. Tax incentives for renewable energy technology
2. Transportation
    a. Mandatory fuel economy standards for road transportation
    b. Taxes on truck purchase, registration, motor fuel, and road use
    c. Investment in public transport and nonmotorized means of transport
3. Buildings
    a. Improvement in appliance efficiency
    b. Increased energy efficiency in building codes

4. Industry
   a. Improvement in performance standards
   b. Subsidies and tax credits for greenhouse gas reduction
   c. Trading of carbon credits
5. Agriculture and Forestry
   a. Financial incentives for improved land management
   b. Efficient use of fertilizers and irrigation
   c. Financial incentives to increase forest area and reduce deforestation
6. Waste Management
   a. Financial incentives for improved waste and wastewater management
   b. Use of waste as a renewable source of energy
   c. Improvement in waste management regulations

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Keywords

adaptation
anthropogenic
asymmetric stretching
atmospheric window
clathrate
contrail
dipole moment
greenhouse effect
greenhouse gases
mitigation
Montreal Protocol
negative feedback
parameterizations
positive feedback
radiative forcing
residence time (T_{res})
sinks
sources
symmetric stretching

Questions and Problems

1. List the three ways the amount of energy in the Earth's atmosphere can be changed.
2. What is a Milankovitch cycle, and how is it involved in the development of an ice age?
3. Describe what is meant by the greenhouse effect.
4. What was the concentration of CO_2 in the atmosphere at the following times:
   a. 20,000 years ago
   b. Measured in Mauna Loa in 1958
   c. Measured in Mauna Loa in 2008

5. List five greenhouse gases.
6. Which gas is considered the most important greenhouse gas?
7. Which historical evidence links atmospheric carbon dioxide concentration with global temperature?
8. List the two most important anthropogenic reasons that tropospheric carbon dioxide concentrations are increasing.
9. What is meant by the term *sequestered carbon?* Give two examples.
10. Why do molecular oxygen and nitrogen, the primary constituents of the troposphere, not absorb IR radiation?
11. Why is water vapor not considered a greenhouse gas, even though it absorbs IR radiation?
12. Describe what is meant by the *atmospheric window.*
13. Describe the molecular characteristics of CH_4 and CO_2 that make them able to absorb IR radiation.
14. What is the residence time of pollutant XY if it has an atmospheric concentration of 6.0 ppm and 300 million tons of it is released into the atmosphere each year? XY has a molecular weight of 50 g/mol.
15. If the residence time of pollutant ZZ is 100 years and its input rate is 5×10^8 kg/year, what is the total amount of ZZ in the atmosphere? ZZ has a molecular weight of 62 g/mol.
16. The amount of water vapor in the troposphere varies depending on the temperature and the location. In this context, describe what is meant by the terms *positive feedback* and *negative feedback.*
17. List two natural sources of tropospheric CO_2 and one anthropogenic source.
18. List three sinks for tropospheric CO_2. Which is the most important?
19. Coal with a high sulfur content burns to produce the expected combustion products from carbon, but it also produces sulfate from burning of the sulfur. Sulfate emitted from smokestacks creates tropospheric sulfate clouds. Which two effects would emissions from this coal combustion have on global warming?
20. List two natural sources of tropospheric methane and one anthropogenic source.
21. List three sinks for tropospheric methane. Which is the most important?
22. What is methane hydrate?
    a. Where can it be found?
    b. What is a clathrate?
    c. Which series of events could lead to the release of methane from methane hydrate?
23. Describe events that could lead to the following:
    a. Increased releases of methane from swamps
    b. Increased releases of methane from methane hydrate
    c. Runaway greenhouse effect
24. What is the major source of tropospheric nitrous oxide?
25. What is the major sink for tropospheric nitrous oxide? What is its atmospheric lifetime?
26. What is the major anthropogenic source of atmospheric CFCs?
27. How do the molecular structures of HCFCs differ from those of CFCs?
28. For IR radiation, give the wavelength range in μm and cm^{-1}.
29. As can be seen in Figure 4.10, methane absorbs radiation at two regions in the IR spectrum: 3 to 4 μm and 7 to 8.5 μm. Which of these absorptions is considered to cause the greenhouse effect? Why?
30. Which of the following molecules would you expect to absorb IR radiation and be greenhouse gases if they were released into the atmosphere by anthropologic events: H_2S, H_2, and Rn?
31. Using information in Table 4.1, compare the greenhouse effect caused today by past releases of methane and Freon 11. Which of the two has the greater effect? Why?

32. Which three factors contribute to radiative forcing?
33. During the industrial period, have the following factors caused a positive or negative radiative forcing?
    a. Carbon dioxide
    b. Atmospheric aerosols
    c. Land use
34. Give three examples of human activities that cause radiative forcing, other than greenhouse gas emissions.
35. Which natural events cause radiative forcing? Are any of these events important today?
36. Aircraft produce persistent linear trails of condensation that are called contrails. Go to http://www.ipcc.ch and find out if contrails cause positive or negative forcing.
37. The manufacture and sale of which greenhouse gases were banned by the Montreal Protocol?
38. Draw the molecular formula of nitrous oxide. Why is this molecule able to absorb IR energy? What is the major source of nitrous oxide in the troposphere?
39. From ice cores taken from Antarctic glaciers, scientists are able to estimate the global temperature at the time that the ice was frozen. Describe how this is done.
40. Climate scientists have developed estimates of global temperatures in the year 2100 if greenhouse gas emissions are not lowered. What temperature increase is expected, and what will be the suspected consequences of that increase?
41. Describe the goals of the Kyoto Protocol with respect to greenhouse gases.
42. How does the Chicago Climate Exchange work?
43. Which two recent advancements have improved climate scientists' ability to predict global climate change?
44. Global climate change will cause significant changes in several ecosystems. Go to http://www.ipcc.ch and find the changes expected in three different ecosystems.
45. Global climate change is predicted to negatively affect human health. Go to http://www.ipcc.ch and find four different ways that human health is expected to be negatively impacted.
46. What was the atmospheric concentration of CO_2 in 2008? What ceiling on atmospheric CO_2 concentration does the IPCC report recommend in the future?
47. Several actions have been suggested to increase (or speed) the Earth's sinks for greenhouse gases. One such suggestion is to seed the warmer parts of the Pacific Ocean with zinc and iron compounds. Explain how this intervention might affect atmospheric greenhouse gas concentration.
48. Ozone is found both in the stratosphere and in the troposphere. What effect on global warming would each of the following changes have?
    a. Increasing stratospheric ozone concentration
    b. Increasing tropospheric ozone concentration
49. Rice fields are an important part of human nutrition but also a major source of greenhouse gas. First determine which greenhouse gas is released from rice paddies. Then go to http://www.ipcc.ch and investigate how changing the soil on which rice is grown might reduce the greenhouse effect.
50. Essay question: Identify four of your behaviors that release greenhouse gases. Explain which gas is released and how this action releases the gas into the troposphere; include products you consume on a regular basis. Suggest behavior modification that could reduce the greenhouse effect.
51. Essay question: Which specific steps should the U.S. government take to reduce greenhouse warming? Does a global institution, such as the United Nations, or a group of industrial nations, such as the G8, need to coordinate action, or should our government act independently to lead the world?